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Use of the Mg-containing quaternary led to a pseudomorphic SCH laser. The graded bandgap ohmic contact reduced threshold voltages to 5 volts as room temperature cw was obtained. TEM studies provided the first reports of compositional modulation in a II-VI alloy. It was found that the quaternary above a certain bandgap exhibited a compositional modulation in a particular <110> direction. Laser degradation has been studied using electroluminescence microscopy and TEM of degraded devices. The microstructural analysis revealed that the degradation originated from stacking faults nucleated at or near the II-VI/III-V interface. Using etching techniques it was determined that room temperature cw lasers had stacking fault densities of $5x10^5$ to $1x10^6 cm^{-2}$. Recently we have emphasized reducing these densities. We have reached the $10^3 cm^{-2}$, and are consistently in the low $10^4 cm^{-2}$. It appears that the high resistivity observed in p-type wide bandgap alloys is the manifestation of a DX-like behavior. Although previous studies reported DX centers in many n-type semiconductors, there are no previous reports for acceptors in any p-type semiconductor; we named this phenomenon an AX center.

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"II-VI/III-V HETEROJUNCTIONS"

by

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Summary of activities in the period covered by this final technical report

a. Pseudomorphic SCH laser structures.

The reporting period of the previous three year grant ended in the time frame when we had just reported the development of the Zn(Se,Te) graded contact scheme for contacting p-type ZnSe. The device configuration developed by the Purdue/Brown group, which had been the focus of developments in the previous reporting period, was a pseudomorphic structure based on ZnSSe where the optical waveguiding was provided by an array of six quantum wells. The rationale behind the configuration was an attempt to avoid the misfit dislocations at the boundary between the cladding and waveguiding regions which were a characteristic of all previous separate confinement heterostructure configurations (SCH). The group at SONY then reported success, at least at low temperatures, with a structure which was the same as the Purdue/Brown structure, but where the alloys used were replaced by wider bandgap compound. The structure was primarily composed of ZnMgSSe where the addition of Mg provided for lattice matching to GaAs with a wider bandgap than had been possible with the ZnSSe used in the Brown/Purdue pseudomorphic structure. The demonstrated usefulness of the Mg-containing alloy led us (**Appendix A**), as well as Philips and 3M to quickly fabricate a separate confinement heterostructure laser in which the quaternary served as cladding layers to ZnSSe optical waveguiding regions bracketing the ZnCdSe quantum well. Using such structures, with a suitable modification to our graded bandgap ohmic contact scheme, we were able to reduce our threshold voltages to 7 volts while increasing the room temperature duty cycles to over 20% before failure. Subsequently (see below), the threshold was reduced to about 5 volts as room temperature cw was obtained.

b. Electron injection at the ZnSe/GaAs heterovalent interface.

As the use of the graded contact scheme significantly reduced the laser operating voltage, it became important to examine the small but finite voltage drop at the ZnSe/GaAs heterovalent interface. Thus, activities in the initial year of the period covered by this report included the study of electron injection at the GaAs/ZnSe heterovalent interface. It was found, in a continuation of ZnSe/GaAs interface studies carried on under a previous AFOSR grant, that the voltage at the heterovalent interface could be reduced by efforts to reduce the interface state density at the ZnSe/GaAs interface by nucleating the ZnSe on a GaAs epilayer having the appropriate surface reconstruction.

c. Compositional modulation in sulfur-containing alloys of ZnSe.

The close ties to TEM provided by the grant resulted in the first reports of compositional modulation in a II-VI alloy. It was found that the quaternary, above a certain bandgap, as well as the ternary ZnSSe (at sufficiently high S fractions), exhibited an anistropic, quasi-periodic compositional modulation in a particular <110> direction. Details of this work are described in

Appendix B of this report.

d. Low voltage, room temperature cw blue/green laser diodes

In the beginning of the second year of the current three year grant we (the Brown/Purdue group), along with SONY, reported the first room temperature cw operation of a blue/green laser diode. In the December 1993 issue of Electronics Letters (**Appendix C**) both the Brown/Purdue group (20 second lifetime) and SONY (1 second) published the first reports of low voltage room temperature CW laser diodes. These remained the only two groups with this capability until the fall of 1994 when Philips also reported room temperature CW for 4 seconds and Matsushita reported 1 second. It is important to note that all the aforementioned groups (plus 3M which currently holds the lifetime record of 3 hours) are currently employing the Zn(Se,Te) heterostructure graded contact scheme (for contacting p-ZnSe) first proposed and demonstrated by the Brown/Purdue group.

e. Degradation of laser diodes.

Since the first reports of room temperature cw operation, the major issue limiting the development of commercial blue/green devices is the degradation occurring in the active region which eventually reduces the gain to the point where lasing ceases. The mechanisms of degradation have been studied by our group using electroluminescence microscopy (primarily at Brown University) to observe the event in real time, followed by transmission electron microscopy of degraded devices (primarily at Purdue) to determine the microscopic mechanisms involved in the degradation.

The microstructural analysis (**Appendix D**) of degraded laser structures revealed that the degradation originated from two causes. The first problem is the presence of stacking faults which generate threading dislocations. These threading dislocations pass through the quantum well region of the laser device and act as nucleation points for the growth of patches of dark line defects. The networks of dislocation dipoles which make up the nonradiative patches grow due to the second problem which is the presence of point defects. The dislocation networks which form the dark patches grow due to a mechanism of nonradiative recombination assisted climb of dislocations associated with the presence of point defects. It is encouraging that initial efforts to reduce the density of point defects have been successful; this does not appear to be an intrinsic problem. The occurrence of stacking faults became the focus of interest for several groups. The occurrence of stacking faults still appears to be of extrinsic origin as, provided correct growth techniques are employed, they are not nucleated within the upper layers of the laser structures, but appear (at current detection resolutions) only in the vicinity of the heterovalent interface between ZnSe and the GaAs buffer layer.

We are pleased to report a significant decrease in the stacking fault density over the past year. First it is necessary to state that our previous estimates of stacking fault densities were low by about a factor of two or three. The previous estimates were based on plan view TEM imaging.

Over the past year we have developed the ability to measure the density of extended defects by counting the density of etch pits. Using the etching technique we determined that our first room temperature cw lasers actually had stacking fault densities in the $5x10^5$ to $1x10^6 cm^{-2}$ range. By employing a variety of techniques, in the last year of the reporting period we had succeeded in reducing the densities of extended defects to a level of mid $10^4 cm^{-2}$, but not consistently. Since the end of the period covered by this report we have reduced the densities of extended defects into the $10^3 cm^{-2}$ range, and are now consistently in the low $10^4 cm^{-2}$. Over the past year we have placed our emphasis on reducing these densities. In the coming months we will resume the growth of laser structures in order to determine how the lifetimes will be extended as a result of the aforementioned reduction in extended defects.

f. The AX center - increasing resistivity with bandgap of alloys of ZnSe doped with nitrogen

The room temperature CW lasers mentioned above operate at approximately 508nm in the blue/green portion of the spectrum. In March 1993 at the spring meeting of the Materials Research Society in San Francisco we reported what at that time was the shortest wavelength operation for a room temperature injection laser at 480nm. Those devices were operated pulsed to about 10% duty cycle and had a threshold voltage of about 9 volts. Since that time we have reported a new laser device, again at the shortest reported room temperature wavelength of 462 nm. These devices have a threshold voltage of 10.5 volts. The increase in operating voltage as the wavelength is reduced appears connected to the increased impedance of the relatively wide bandgap cladding layers of these pseudomorphic separate confinement heterostructure lasers. In temperature dependant Hall measurements (made possible by the fact that the Zn(Se,Te) graded contact remains ohmic down to cryogenic temperatures) we have determined the acceptor activation energies in our films. The activation energy is observed to increase rapidly as the bandgap is increased in going from ZnSe to ZnSSe, and then to ZnMgSSe. Although our previous studies have indicated that nitrogen in ZnSe behaves as a hydrogenic impurity, the observed increase in activation energy with bandgap is quite inconsistent with an effective mass model for a hydrogenic impurity. In the third year of the reporting period we were able to provide an explanation for this previously puzzling phenomenon. It appears that the apparent high activation energy (hence resistivity) observed in the wide bandgap alloys is the manifestation of a DX-like deep center behavior. Details are to be found in the copy of a Applied Physics Letters reprint in **Appendix E**. It is of particular interest to note that, although scores of studies have been reported on DX centers in n-type semiconductors of all types, there has been no previous report of such behavior for acceptors in any p-type semiconductor; we have called this phenomenon an AX center. Besides the implications for short wavelength lasers, this discovery has had some considerable impact on semiconductor theorists having interest in such issues.

Serial Journal Articles (contributed and invited)
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APPENDIX A

Pseudomorphic separate confinement heterostructure blue-green diode lasers

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The growth and performance of pseudomorphic separate confinement heterostructure blue-green laser diodes are described. The devices incorporate the (Zn,Mg)(S,Se) quaternary as cladding layers surrounding a Zn(S,Se) waveguiding layer, and having single or multiple quantum wells of (Zn,Cd)Se. Devices have been operated at room temperature under pulsed conditions ($\sim 1\ \mu s$, 10^{-3} duty cycle) for periods up to 1 h. X-ray rocking curve full width at half-maxima as low as 44 arcsec were obtained for a laser structure employing quaternary cladding layers (Mg=9%, S=12%), consistent with transmission electron microscope observations showing no dislocations or stacking faults. The Zn(Se,Te) graded contact was adapted to form an ohmic contact to the top *p*-type quaternary layer.

Following the first demonstrations of the blue-green diode laser,[1,2] further developments of the ZnCdSe/ZnSe/ZnSSe single-(SQW) and multiple-quantum-well (MQW) devices have included pulsed room temperature[3] and cw operation at 77 K.[4] Over this temperature range, the emission wavelengths vary typically from about 470 to 520 nm. Subsequently, several other groups have also reported diode laser operation at cryogenic temperatures in either identical or very similar ZnSe-based structures.[5–7] In an interesting recent development, a group at Sony Research Center employed a wider band gap quaternary (Zn-,Mg)(S,Se) as the barrier layer material to shift the emission wavelength of a ZnSe/(Zn,Mg)(S,Se) MQW laser (which was operated at 77 K) to 495 nm.[8]

In this letter we describe techniques for the growth of the (Zn,Mg)(S,Se) compound by molecular beam epitaxy (MBE), and the incorporation of the quaternary in a pseudomorphic separate confinement heterostructure (SCH) diode configuration designed to explore the opportunities presented by this alloy. In contrast to the previous blue/green diode laser designs, the potential advantages afforded by the quaternary lie in the direction of providing the enhanced optical confinement of the SCH configuration, while at the same time preserving a pseudomorphic structure. Our SCH devices have been operated at room temperature with pulsed excitation ($\sim 1\ \mu s$, 10^{-3} duty cycle) for periods up to 1 h. (Previous devices typically failed after 2–3 min at room temperature.) Philips Laboratories has recently obtained nearly 400 K operation with 10–50 ns pulses in a similar structure.[9] It appears that this quaternary compound, given the advantages of a considerably more flexible heterostructure design, could provide the key to achieving room temperature cw laser operation.[10]

A Perkin–Elmer 430 modular MBE system with separate II-VI and III-V growth chambers was employed in this study. The laser structures were grown on homoepitaxial (100) GaAs buffer layers. The cladding, confinement, and QW layers were grown in a II-VI growth chamber with elemental Zn (6*N*), Se (6*N*), and Cd (6*N*) from Osaka Asahi, ZnS (6*N*) from Sumitomo, and Mg (4*N*) from Cerac. Zn(Se,Te) graded contact layers, which we reported recently as a low-resistive ohmic contact to *p*-type Zn(S,Se),[11] were grown in a second II-VI chamber.[12] Sticking coefficient ratios among the constituent elements, derived from the measurement of fluxes (using a quartz crystal monitor) and quaternary compositions from several epilayers, were used to control the alloy fractions. Substrate temperatures were monitored during growth by an infrared pyrometer which was calibrated in advance from the oxide desorption temperature (582 °C) of (5 H_2SO_4 : 1 H_2O_2 : 1 H_2O) etched GaAs substrates (in the III-V growth chamber). Various structural configurations and growth parameters were explored. One variation between samples was the growth temperature of the different II-VI layers. In some structures the growth temperature was maintained at 260 °C throughout; in other structures the (Zn,Mg)(S,Se) cladding layers were grown at 260 °C, while the Zn(S,Se) and (Zn,Cd)Se layers were grown at 245 °C. For the growth of all the II-VI compounds, the flux ratios were adjusted to maintain a barely anion-stabilized surface, as evident by a diffuse (2×1) surface reconstruction. The growth rate of the quaternary was 0.5 μm/h as confirmed by both selective wet etching and transmission electron microscope (TEM) imaging. A solid $ZnCl_2$ source and a rf nitrogen plasma cell were used to provide *n*-type (Cl doped) and *p*-type doping, respectively, for the II-VI compounds. The typical doping levels in the Zn(S,Se) layers were similar to those of previous laser devices.[13] The hole concentration, as determined from Hall measurements using the aforementioned graded ohmic contacts, was $3.3\times10^{16}\ cm^{-3}$.

The conditions for the growth of the quaternary epilayers were derived through an iterative procedure, with structural quality evaluated by x-ray diffraction rocking

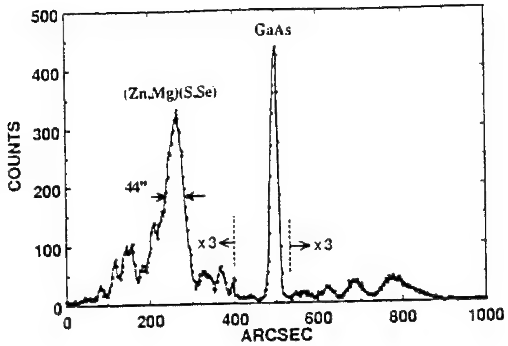

FIG. 1. X-ray rocking curves of a laser structure employing $Zn_{0.91}Mg_{0.09}S_{0.12}Se_{0.88}$ quaternary cladding layers. The features appearing on the high-angle side of GaAs are attributed to the Zn(S,Se) region. The dimensions of the sample structure are shown in the inset of Fig. 3.

curve analysis and cross-sectional TEM. The alloy fractions were measured using a CAMECA SX50 electron microprobe the conventional energy dispersive x-ray spectroscopy (EDX) technique was found not applicable due to the relatively weak intensity of the Mg fluorescence. Photoluminescence measurements were used to determine the band gap of the quaternary.

X-ray rocking curves were measured using a four crystal Si monochrometer. Narrow rocking curves were obtained over a range of alloy fractions corresponding to a lattice mismatch to GaAs of up to 0.23%, and where the quaternary layers were under compression. The absence of dislocations in cross-sectional images indicated the pseudomorphic nature of the layers whose thicknesses were in excess of 0.75 μm. Full width at half-maximum (FWHM) values of as low as 44 arcsec were obtained for a laser structure with the waveguiding and QW regions grown at 245 °C. (The dimensions of the SCH SQW laser structure are shown in the inset of Fig. 3.) The features at the higher-angle side of the GaAs peak are likely from the Zn(S,Se) confinement layers (thickness=4000 Å). Simulations using dynamical theory suggest that these multiple peaks are due to reflection interference from the (Zn,Mg)(S,Se)/Zn(S,Se) interfaces. The features surrounding the main diffraction peak (FWHM=44 arcsec) of the (Zn,Mg)(S,Se) cladding layers (at the lower-angle side) are likely due to a slight unintentional drift of the growth parameters which results in a small change in alloy fractions. As was previously discussed for InGaAsP,[14] x-ray features related to those we observed were theoretically explained in terms of a slight drift in alloy fraction. Layers under tension tend to exhibit surface lines or cracks lying in both ⟨110⟩.

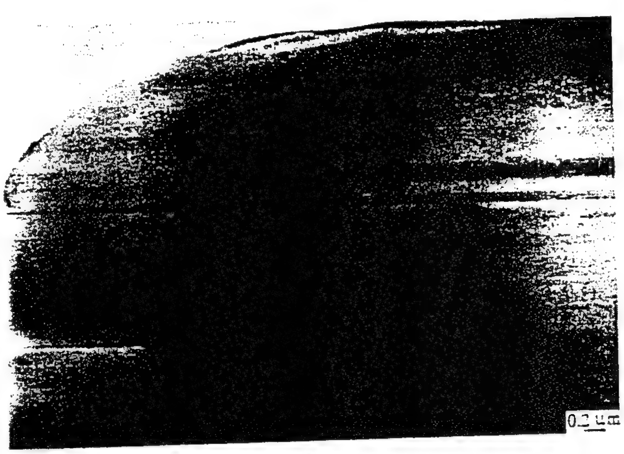

FIG. 2. Cross-sectional bright-field TEM image of a laser structure grown on a GaAs buffer layer.

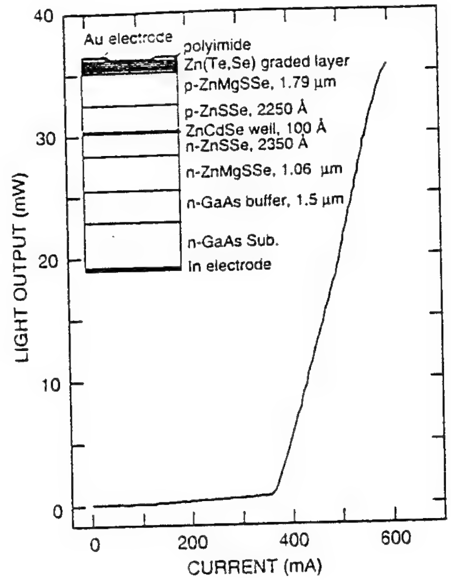

FIG. 3. Pulsed output power vs injection current for a 1000-μm-long device. The electrical excitation is applied in 500 ns pulses at a repetition rate of 5 kHz. A schematic diagram of the laser structure is shown in the inset, the dimensions shown were determined from a TEM image.

The bright-field cross-sectional TEM image of a SQW laser structure is shown in Fig. 2. The absence of threading/misfit dislocations and stacking faults, which is qualitatively consistent with the measured x-ray FWHM of 44 arcsec, indicates that the II-VI laser structure is pseudomorphic to the GaAs epilayer.

The heterostructures were fabricated into gain guided laser devices with cleaved end facets defining resonators of lengths ranging from 500 to 1500 μm. Stripe widths of 20 μm were used to laterally define the current to approximately this dimension (though current spreading up to 10 μm was evident in the active region). The devices were mounted on ceramic blocks with the GaAs substrate in contact with the block. The lasers have been operated over a range of temperatures: in this letter we focus on their performance at room temperature only. The electrical excitation was pulsed, ranging from ≈ 1 μs to 100 ns in duration, at repetition rates of 1–10 kHz. In many devices the gain guiding was sufficient to limit the spatial output to a single or nearly single transverse mode of the laser, especially near the threshold. The device lifetime varied depending on the electrical pulse width and the duty cycle. At a duty cycle of 10^{-3} and pulse width of 1 μs we have operated the devices for more than 1 h. For brief periods of time (on the order of seconds), duty cycles in excess of 10% have been reached.

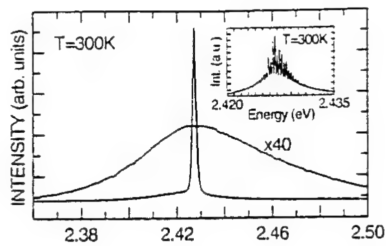

FIG. 4. Output spectra of 500-μm-long laser devices below and above threshold, showing the spectra relationship between spontaneous and stimulated emission. The inset shows the spectra (under higher resolution) slightly above threshold, displaying the longitudinal mode content.

Figure 3 shows the room temperature emission characteristics of a 1000-μm-long SCH SQW device (shown in the inset) which was grown entirely at 260 °C, as a function of the input current. The output power refers to integrated optical pulse energy divided by the individual current pulses. The actual optical power is higher by as much as 30% due to the nonrectangular shape of the laser pulse. We have observed that the threshold current density is nearly inversely proportional to the resonator length in such a fashion that, while the largest loss in the lasers is due to the end facet reflectivity, substantial attenuation due to absorption and scattering is also present. The threshold current density is approximately 1.8 kA/cm^2, somewhat higher than what we obtained earlier with (Zn,Cd)Se/Zn(S,Se) MQW diode lasers with high reflectivity coated facets at room temperature.[4] In principle, however, the (Zn,Mg)(S,Se) quaternary optical cladding layers should be advantageous in that, due to the larger band gap (band edge emission of 2.972 eV from PL at 10 K for 9% Mg and 12% S), attenuation by the absorption tails of the alloy is expected to be reduced. Typical laser threshold voltages at room temperature were about 12–13 V in these initial structures. Structures with three QWs comprising the active region have shown threshold current densities of 1.8 kA/cm^2. These structures also demonstrated slope efficiencies of 0.26 W/A.

The room temperature spectral characteristics of a SCH SQW heterostructure are shown in Fig. 4. The figure displays the edge emission spectra above and below the laser threshold, centered at a wavelength of approximately 515 nm. The inset shows details of the laser spectrum slightly above threshold, including the presence of well-defined longitudinal modes. Depending on the duration and duty cycle of the current pulse, more complex modal behavior can occur, indicative of the presence of competing transverse modes. By time resolving the emission characteristics, we have also observed that the devices are quite sensitive to gain-switching effects which also vary in their detail from device to device, depending on the electrical impedance of the particular diode. For example, for a 1 μs current pulse, the laser output can consist of several temporally distinct pulses of shorter duration, especially as the device deteriorates. In the limit of short electrical pulse (<100 ns), we have observed gain-switched behavior, with short optical pulses (~ 1 ns) and high peak powers (hundreds of mW) generated by the devices.

In summary, pseudomorphic (Zn,Mg)(S,Se)/Zn(S,Se)/(Zn,Cd)Se QW SCH lasers have been grown, fabricated, and characterized at room temperature under pulsed conditions. With the SCHs, significant progress has also been made in the reduction of the voltage necessary for reaching the laser threshold. Extending the use of the graded gap contact to index guided mesa devices has led to observation of lasing at voltages as low as 7 V.[15]

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APPENDIX B

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Phase separation in $ZnSe_{1-x}S_x$ and $Zn_{1-y}Mg_ySe_{1-x}S_x$ layers grown by molecular beam epitaxy

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Abstract

The occurrence of phase separation in (100) $ZnSe_{1-x}S_x$ and $Zn_{1-y}Mg_ySe_{1-x}S_x$ layers grown by molecular beam epitaxy was found by transmission electron microscopy. The direction of the phase separation is [011], and the period of the composition modulation ranges from 300 to 500 Å. X-ray microanalysis of the two regions resulting from the phase separation showed one to be sulfur-rich and the other sulfur-deficient. The one-to-one correspondence of the wavy surface structure and the composition modulation suggests that the phase separation occurs via nonuniform incorporation of sulfur atoms into the wavy growth plane of the epilayer.

The employment of ternary $ZnSe_{1-x}S_x$ and quaternary $Zn_{1-y}Mg_ySe_{1-x}S_x$ phases has led to recent significant progress of blue-green diode lasers [1–3]. These alloy phases provide considerable flexibility for designing laser structures under the restriction of lattice matching to the GaAs substrate crystal. Room temperature laser operations under pulsed conditions (1 μs, 10^{-3} duty) have been achieved for up to 1 h by using pseudomorphic structures in which ternary and quaternary layers serve as wave guiding and cladding layers, respectively [3].

During the course of the transmission electron microscope (TEM) analysis of laser structures grown by molecular beam epitaxy (MBE), we have found phase separation in a number of the ternary and quaternary layers. The phase separation occurred nearly along the [011] direction in the (100) epilayers. By X-ray microanalysis, the phase separation was found to be periodic changes of Se and S concentrations. Up to the present, phase separation has been observed in many III–V alloy epilayers [4]. To our knowledge, however, there are only few cases of phase separation in II–VI alloy epilayers [5]. The occurrence of phase separation may have significant implication to the development of laser structures based on these II–VI alloy phases. It is known to affect transport and optical properties [4]. Earlier studies on light emitting devices based on InGaAlP also suggest that phase separation may make the device more degradation resistant [6]. In this paper, we present TEM studies of phase separation in these II–VI alloy layers, including results of X-ray microanalysis.

The ternary and quarternary epilayers and laser structures containing alloy layers were grown

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at temperatures ranging from 245 to 260°C on (100) GaAs by using a Perkin-Elmer 430 modular MBE system with elemental Zn, Se and Mg sources and a ZnS source. The total cation-to-anion flux ratio was adjusted to maintain a barely anion-stabilized growth surface, as evidenced by a diffuse (2×1) surface reconstruction. Average compositions of quaternary epilayers were determined by using a Cameca SX50 electron microprobe. Average compositions of ternary layers in laser structures were estimated based on the flux conditions and X-ray rocking curve measurements. A JEM 2000EX transmission electron microscope and a JEM 2000 FX analytical electron microscope were used for examination of microstructures. Cross-sectional samples with two orthogonal $\langle 011 \rangle$ directions and plan-view samples were prepared by ion milling. The convergent beam electron diffraction technique was employed in order to identify the [011] and $[01\bar{1}]$ directions of cross-sectional samples [7].

A series of laser structures and alloy epilayers were examined by TEM observations of [011] and $[01\bar{1}]$ cross-sectional samples. Among those layers, all quaternary epilayers with sulfur concentrations greater than $x = 0.2$ exhibit strong phase separation. About one half of the $ZnSe_{1-x}S_x$ layers with $x \approx 0.07$ were found to have phase separation. In quaternary layers with sulfur contents close to $x = 0.12$, no clear image of phase separation was observed; some layers appear to exhibit very weak contrasts of phase separation.

Figs. 1a and 1b are $\bar{2}00$ dark field images of $[01\bar{1}]$ and [011] cross-sectional samples of a $Zn_{1-y}Mg_ySe_{1-x}S_x$ epilayer. The average composition of this epilayer is $x = 0.218$ and $y = 0.075$. The narrow bright band seen along the interface with the GaAs substrate is a thin ZnSe layer. Both images show many stacking faults originating at the interface region. They are believed to be caused by the lattice mismatch between the epilayer and the GaAs substrate. Ternary and quaternary layers in laser structures whose compositions were selected to give rise to close lattice matching to GaAs, however, were found to be nearly free from these defects [3]. In the image of the $[01\bar{1}]$ cross-section, a periodic array of bright and dark bands parallel to the growth direction are seen from the bottom to the top of the quaternary epilayer. The period of this modulation is about 450 Å. In the image of the [011] cross-section, on the other hand, no such periodic modulation is observed, suggesting that the modulation is one-dimensional and parallel to the [011] direction. Fig. 2 is a 020 dark field image of a plan-view of the same quaternary epilayer. A highly regular periodic array of bright and dark bands is seen in the image. Directions of bands are nearly parallel to the $[01\bar{1}]$ axis. Widths of bright and dark bands are not equal to each other; the former is about 80 Å and the latter 370 Å. Dark segments in the image are due to defects in the epilayer.

Fig. 3 is a bright field image of a $[01\bar{1}]$ cross-

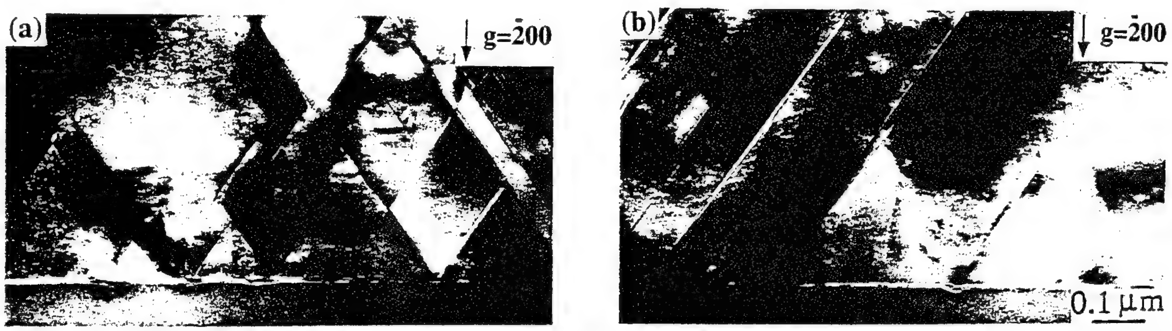

Fig. 1. $\bar{2}00$ dark field images of (a) a $[01\bar{1}]$ cross-section and (b) a [011] cross-section of a $Zn_{1-y}Mg_ySe_{1-x}S_x$ ($x = 0.218$ and $y = 0.075$) epilayer.

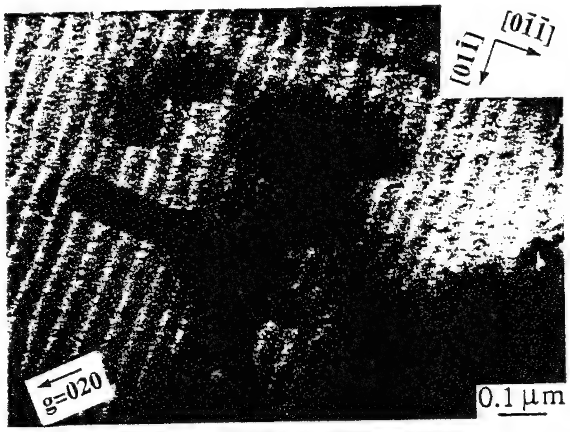

Fig. 2. 020 dark field image of a plan-view sample of a $Zn_{1-y}Mg_ySe_{1-x}S_x$ ($x = 0.218$ and $y = 0.075$) epilayer.

section of a laser structure containing $ZnSe_{1-x}S_x$ ($x \approx 0.07$) layers. In the image, a periodic array of bright and dark bands due to phase separation is seen in the lower portion of the $ZnSe_{1-x}S_x$ layer where Cl was doped as donors. In the upper portion of the $ZnSe_{1-x}S_x$ layer where N was doped as acceptors, the contrast modulation due to phase separation is also seen, but its contrast is much weaker than that in the lower portion. The same trend, i.e., clearer images of phase separation in n-type layers than in p-type layers, was observed in all laser structures in which phase separation was found. The image of the phase separation was observed far more clearly in the quaternary layers with the sulfur concentrations greater than $x = 0.2$ than in other layers, so that detailed analyses of phase separation were carried out by using these quaternary layers. The X-ray microanalysis of compositions in bright and dark bands was carried out on the plan-view sample shown in Fig. 2 by using a JEM 2000 FX analytical microscope. Concentrations of Se and S in each band were directly estimated by using the intensity ratio of the Kα radiation of Se and the K radiation of S, following the proportional relationship between the characteristic X-ray intensity and the concentration for thin specimens [8]. The average compositions of the epilayer was also used for the estimation. By this analysis, the sulfur concentrations in the bright and dark bands were found to be $x \approx 0.13$ and $x \approx 0.23$, respectively. The change of the Mg concentration and, hence, the change of the Zn concentration, was not detected because of the inability to observe an X-ray peak of Mg. The intensity of the X-ray radiation of Zn relative to those of Se and S did not exhibit any systematic change between the two bands.

Figs. 4a, 4b and 4c are dark field images taken from the same area of a [01$\bar{1}$] cross-sectional sample of the quaternary epilayer by using 200, 400 and 022 reflections, respectively. The change of the contrast of the periodic modulation is

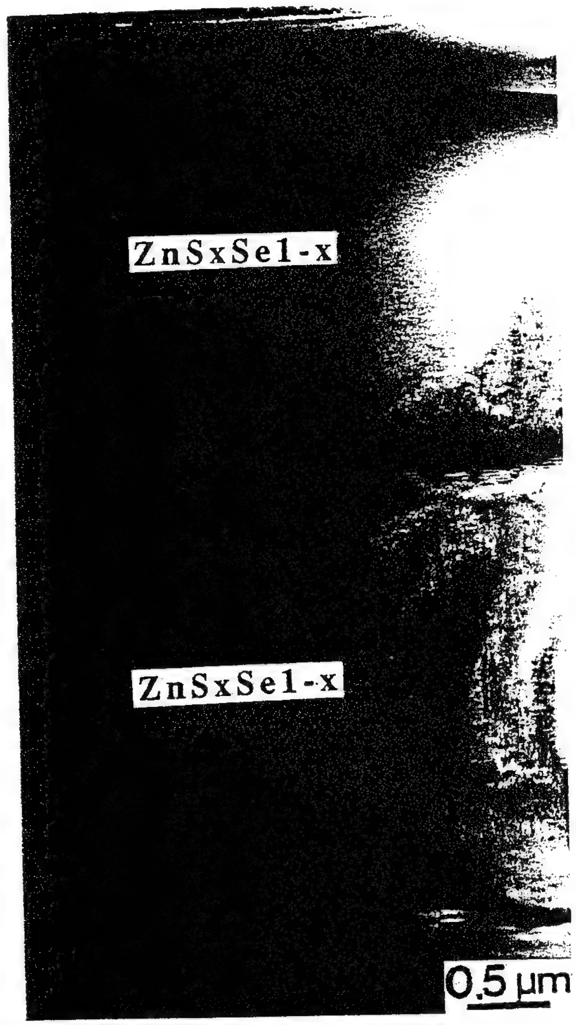

Fig. 3. Bright field image of a [01$\bar{1}$] cross-section of a laser structure containing $ZnSe_{1-x}S_x$ ($x \approx 0.07$) layers.

consistent with the result of the X-ray microanalysis. The 200 dark field image, which is the most sensitive to the change of the composition within one sublattice of the zinc-blende type structure, exhibits the clearest image of the modulation. The 022 image also exhibits clear contrasts of the modulation, which is explained by the change of the spacing of (022) lattice planes due to the change of the sulfur concentration. The 400 image, on the other hand, does not show any significant contrast of the modulation. The absence of the contrast in this image is attributed to the fact that the spacing of (h00) type lattice planes is not affected by this phase separation and the crystal structure of the 400 reflection is not sensitive to the composition change within one sublattice.

The results described above clearly indicate that phase separation can occur in $ZnSe_{1-x}S_x$ and $Zn_{1-y}Mg_ySe_{1-x}S_x$ epilayers grown by MBE. The X-ray microanalysis has shown that the phase

Fig. 4. Dark field images of a [01$\bar{1}$] cross-section of a $Zn_{1-y}Mg_ySe_{1-x}S_x$ ($x = 0.218$ and $y = 0.075$) epilayer. Reflections used are (a) 200, (b) 400 and (c) 022.

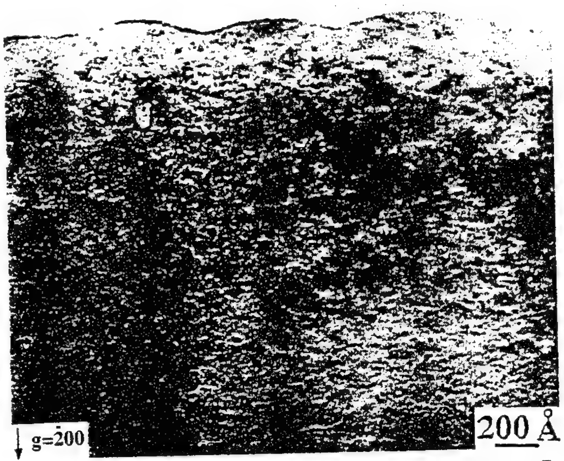

Fig. 5. Bright field image of a free surface region of a [01$\bar{1}$] cross-sectional sample of a $Zn_{1-y}Mg_ySe_{1-x}S_x$ ($x = 0.218$ and $y = 0.075$) epilayer.

separation is described as the formation of S-rich and S-deficient bands. To date, there has been only one report on an experimental study of the phase stability of the $ZnSe_{1-x}S_x$ system, which suggests that this alloy system is completely miscible at 900°C [9]. It is also interesting to note that, according to the delta lattice parameter (DLP) model [10], the $ZnSe_{1-x}S_x$ system is expected to be completely miscible at the temperature used in the MBE growth of the ternary and quaternary layers. The present results, however, suggest strong possibility that these ternary and quaternary systems tend to become immiscible at the MBE growth temperature as the sulfur concentration increases.

There are some unusual features of phase separation in these alloy layers. Compared to compositional modulations resulting from phase separations in III–V alloy epilayers, the modulation in the present case is highly regular and its period is extremely large. Periods of compositional modulations in III–V alloy layers grown by MBE are typically several tens of ångströms, which are expected from surface diffusion lengths during the MBE growth of III–V alloy layers [11]. The very large periods of the modulation in the present case cannot be explained by surface diffusion of atoms if one considers the growth temperature of these II–VI alloy layers. There is one observation which suggests a possible mechanism for the formation of the compositional modulation. TEM images of [01$\bar{1}$] cross-sectional samples of quaternary epilayers having phase separation show wavy surface structures of the epilayers. Fig. 5 is a bright field image showing such a wavy surface structure. As seen in Fig. 5, the period of the wavy surface structure exactly matches that of the compositional modulation. At each hill of the surface a sulfur-deficient band ends, and each valley of the surface matches a sulfur-rich band. Based on this observation, the following mechanism is suggested. Sulfur is a highly volatile species and, hence, is likely to attach only to step and kink sites during the MBE growth. The wavy surface structure, on the other hand, results in a periodic variation of the step density; the step density decreases at the hill and increases at the valley region. The wavy surface structure, therefore, may result in nonuniform incorporation of sulfur atoms and, hence, lead to the compositional modulation. It is unclear at present how such wavy surface structures have formed only in certain epilayers. Further studies are needed to clarify the origin of phase separation in these II–VI alloy layers.

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APPENDIX C

$$p_1 \simeq -\frac{1}{R_L C_L} \tag{6}$$

$$p_{2,3} \simeq \pm j \frac{1}{\sqrt{L_p C_l}} \tag{7}$$

Actually, p_1 is the pole of eqn. 1, where parasitic elements L_p, C_l and R_l are ignored. In reality, $p_{2,3}$ are the imaginary poles of the LC resonance circuit composed of L_p and C_l.

Compensation circuit: Several methods may be applied to overcome the ringing problem. One is to reduce the parasitics by using double bonding, thick bonding wires, or advanced packaging.

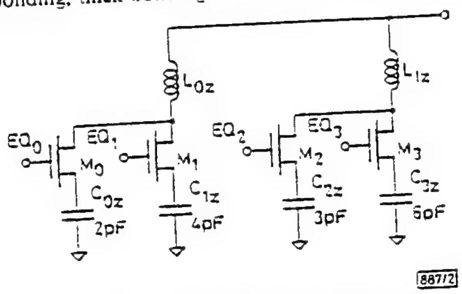

Fig. 2 *New compensation circuit for reducing settling time*

Another is to introduce a circuit compensating the high-Q poles by making a shunt path between the output node and GND. Fig. 2 shows the new compensation circuit inserted between node i and GND. This circuit acts as an RLC series circuit, where the effective R, L and C are R_Z, L_Z and C_Z, vice versa. This circuit makes a shunt path between the output node and GND around the resonance frequency. Therefore, the effect of the high-Q poles is minimised and the peaking in the frequency response is reduced. The effective R_Z, L_Z and C_Z are controlled by the control signals EQ_0, EQ_1, EQ_2 and EQ_3. To cover a broad range of the parameters of inductance and capacitance, the circuit is made programmable. Transistors M_0, ..., M_3 actually act as a resistor, when turned on. The optimal condition is found under the actual test environment. This condition can be programmed into the device in the fabrication stage, or the user can find this for the specific application.

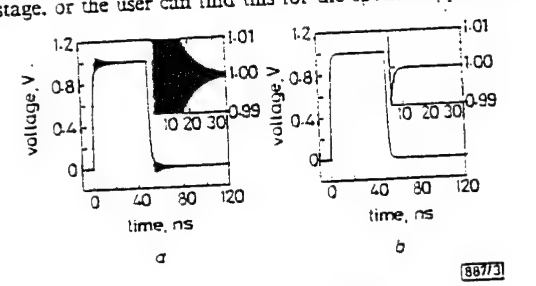

Fig. 3 *Comparison of settling time characteristics*

a Without compensation circuit
b With compensation circuit
$R_l = 1.0$MW, $C_l = 6.0$pF, $L_p = 4.0$nH, $C_L = 20.0$pF,
$R_Z = 20.0$W, $C_Z = 4.0$pF, $L_Z = 7.0$nH

Fig. 3*a* shows the step response of the uncompensated circuit. Fig. 3*b* shows the step response of the compensated circuit. The settling criterion for the 10 bit DAC is 0.05%. The settling time of the uncompensated circuit is 36.5 ns which is reduced to 8.2ns for the compensated case. If L_p were 0, the settling time would be 5.7ns.

This compensation circuit was implemented using a standard CMOS process; a microphotograph of the circuit is shown in Fig. 4. The spiral inductor was made by two layers of metal [3].

Conclusion: The parasitic inductance of a bonding wire and the lead frame causes a ringing at the output node, and increases the settling time. To reduce the settling time, a new compensation circuit was developed which is programmable to cover a broad range of parameter changes. This circuit was applied to the output node of a 10bit CMOS DAC.

Acknowledgment: The authors would like to thank S.-K. Kim, M. Choi and M. Song for various contributions to this work.

Fig. 4 *Microphotograph of implemented compensation circuit*

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Continuous-wave, room temperature, ridge waveguide green-blue diode laser

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Indexing terms:

Continuous-wave (CW) operation of ridge waveguide quantum well diode lasers in the green/blue has been demonstrated at voltages as low as 4.4V in ZnCdSe/ZnSSe/ZnMgSSe pseudomorphic separate confinement heterostructures, with output powers up to 10mW.

Since their inception in 1991, the blue-green diode lasers based on II-VI compound semiconductors have witnessed rapid development. One milestone was reached very recently with the reported demonstration of brief CW laser operation in ZnSe-based quantum well (QW) devices at room temperature, where high reflectivity resonator facet coatings and efforts at efficient heatsinking were employed to reach the conditions necessary for lasing [1]. Furthermore, the electrical bias necessary for laser operation was high, especially in terms of the threshold voltage (V_{th} = 17 V). The large electrical loading that these bias conditions imply is incompatible with technologically viable lasers, especially as they lead fundamentally to very rapid degradation of the components. By adapting a particular scheme for improved electrical contacting, we have recently shown that it is possible to reduce the operating voltage of an index guided, ridge-waveguide diode laser to values of $V_{th} \simeq 7$V [2]. Here we show that continuous wave operation at room temperature can be obtained from these types of device, without resorting to facet coatings, at voltages as low as V_{th} = 4.4V.

The diode lasers described below were separate confinement devices (SCH) where molecular beam epitaxy (MBE) was used to grow the pseudomorphic $Zn_{1-x}Cd_xSe/ZnS_ySe_{1-y}/Zn_{1-z}Mg_zS_wSe_{1-w}$ *pn*-junction heterostructures on *n*-type homoepitaxially grown GaAs buffer layers. Initial reports on gain guided devices based on this

II-VI material scheme [3, 4] were followed by the demonstration of low threshold current, high duty cycle pulsed operation in index guided structures [5], the latter aided by high reflectivity facet coatings. In particular, the approach in [4] included the application of low resistance graded gap ZnSeTe contacts [6, 7] to the topmost p-ZnMgSSe layer.

In the present devices, the Cd concentration in the 75Å thick active $Zn_{1-x}Cd_xSe$ QW layer was $x = 0.20$. The sulphur concentration in the ternary ZnS_ySe_{1-y} was $y = 0.07$ and $y' = 0.12$ in the $Zn_{1-z}Mg_zS_{y'}Se_{1-y'}$ quaternary layer in which the Mg concentration was $z = 0.09$. The active layer was sandwiched between the p- and n-type layers of ZnSSe of ~1200Å thickness, respectively. The outer p-and n-type cladding layers of ZnMgSSe were ~0.80µm thick. A 1100Å thick n-type ZnSSe transition layer was also grown adjacent to the n-GaAs buffer layer. Other details of the growth and characterisation as well as material parameters can be found in [4], including the p-ZnSeTe graded bandgap contact layer to which the PdAu top electrode was applied. Transmission electron microscopy was used to verify that the pseudomorphic conditions were indeed reached, i.e. that no significant density of dislocations was present. The material was processed to ~4–4.5 µm wide ridge waveguide devices by a selfaligned technique employing dry etching and SiO_2-polyimide planarisation. Special attention was paid to perform all the processing steps well below the MBE growth temperature (T_s = 250–300°C). The depth of the etched region reached to within 2500Å of the active QW region. A scanning electron microscope image of a device is shown in Fig. 1, displaying the cleaved facet. Typical resonator lengths of the devices were 500µm to 1mm and no reflective facet coatings were employed. The devices were mounted with the GaAs substrate in contact with a Cu block, an arrangement which provided only a limited amount of useful heatsinking.

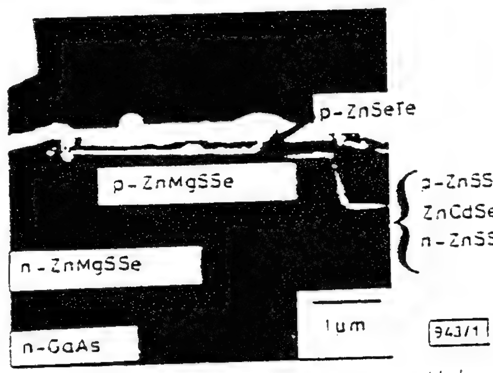

Fig. 1 *Scanning electron micrograph of ridge waveguide laser device*

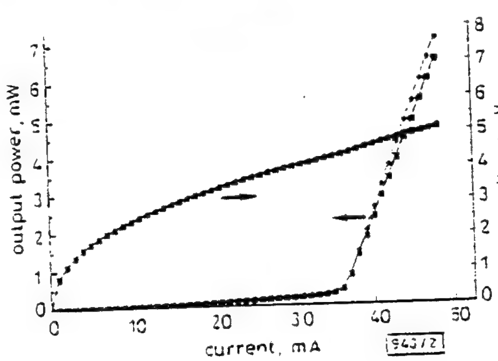

Fig. 2 *Optical output power against current and voltage against current for two room temperature devices under CW conditions*

Data points are connected by lines to guide the eye: no reflective facet coatings were applied
T = 300K. Index-guided laser
● device 1
■ device 2

Fig. 2 shows both the light output and current-voltage characteristics of two 4.3µm wide devices at room temperature under a CW electrical bias. The lasing threshold in these 1000µm long devices was reached at a current I_{th} = 35mA and voltage V_{th} = 4.4V. The devices were nominally identical: the slight difference in their output is probably due to small fluctuations in the processing. The measured differential quantum efficiency is η = 22% per facet, which is somewhat lower than that obtained under low duty cycle pulsed excitation (η = 25% per facet). The threshold current densities in our devices have ranged from J_{th} = 600 to 1100A/cm², depending on the cavity length. (Threshold currents down to 20mA have been measured in 500µm long devices.) Under the CW conditions, output powers up to 10mW have been measured. While the threshold voltage shown in Fig. 2 represents a major advance over previous results, we believe that further improvement is still possible as better understanding is being sought for vertical transport and gain mechanism in these heterostructures.

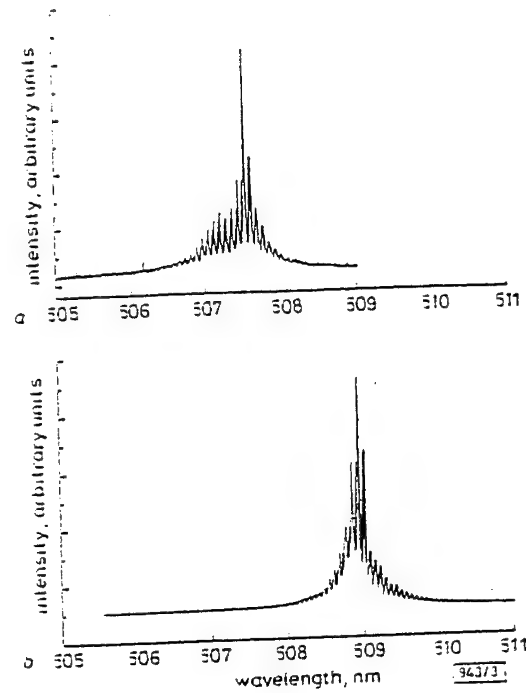

Fig. 3 *Comparison of emission spectra between pulsed, low duty cycle (10^{-3}) operation and CW lasing at room temperature for the injection currents indicated*

a Pulsed, T = 300K, I = 27mA
b CW, T = 300K, I = 25mA

Fig. 3 displays examples of the well defined longitudinal mode spectra typical for our devices, compared here for a 500µm long device under pulsed low duty cycle (10^{-3}) and CW conditions. Single transverse mode operation was routinely obtained. The CW emission wavelength is centred at λ = 508.8nm and is hence redshifted by Δλ = 1.4nm when compared with pulsed emission. This indicates that, on the average, the lattice temperature in the active region is approximately only 20–25°C higher under CW conditions. These first devices have lased in excess of 20s before failure in the CW mode, indicative of the importance of defect generation and degradation in the high current density and high optical intensity ambience, a subject of current studies.

In summary, we have demonstrated a low voltage, continuous-wave room temperature green/blue diode laser by taking advantage of an ohmic contact scheme, a pseudomorphic separate confinement heterostructure, lateral optical confinement, and low temperature processing. The low threshold voltage, in particular, is encouraging from the viewpoint of the further development of these sources towards technological reality.

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APPENDIX D

Microstructure study of a degraded pseudomorphic separate confinement heterostructure blue-green laser diode

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The microstructure of a degraded II-VI blue-green laser diode based on the ZnCdSe/ZnSSe/ZnMgSSe pseudomorphic separate confinement heterostructure has been examined by transmission electron microscopy. Triangular nonluminescent dark defects observed in the laser stripe region by electroluminescence microscopy have been identified to be dislocation networks developed at the quantum-well region. The dislocation networks have been observed to be nucleated at threading dislocations originating from pairs of V-shaped stacking faults which are nucleated at or near the II-VI/GaAs interface and extending into the n-ZnMgSSe lower cladding layer.

Since the first blue-green lasers and light-emitting diodes based on wide band gap II-VI semiconductor materials grown by molecular beam epitaxy (MBE) were realized in 1991,[1–3] effort has been directed at obtaining low threshold current and voltage, high output power, and long lifetime of the devices. A ZnCdSe/ZnSSe/ZnMgSSe separate confinement heterostructure (SCH) appears, at this time, to be the most promising structure for II-VI blue-green laser devices.[4–6] cw laser operation for a lifetime exceeding 20 s at room temperature has been reported for a ridge waveguided laser device based on such heterostructures.[7]

Guha *et al.* were the first to report the microstructure of a degraded blue-green light-emitting device based on the ZnCdSe/ZnSSe single confinement structure, although not operating as a laser.[8] In this letter we report a detailed microstructural study of a particular degraded gain-guided laser device based on the ZnCdSe/ZnSSe/ZnMgSSe pseudomorphic SCH structure carried out by transmission electron microscopy (TEM). We have found that triangular nonluminescent dark defects, which we first observed by electroluminescence (EL) microscopy, and which are clearly related to device degradation, consist of a patch of a dislocation network developed at the active quantum-well (QW) region. By using TEM stereo microscopy, it has been found that the dislocation networks are nucleated at threading dislocations originating from pairs of V-shaped stacking faults. The stacking faults are nucleated at or near the II-VI/GaAs interface.

The gain-guided laser device was fabricated from a ZnCdSe/ZnSSe/ZnMgSSe pseudomorphic SCH structure which is similar to the structure we reported before[7] except that the current structure has three QWs. Transparent indium-tin-oxide (ITO) contacting material was deposited as the contact for the 20-μm-wide and 1-mm-long laser stripe. The device was kept at 11 V for 15 min with a duty cycle of 4%, resulting in an injected current density estimated to be 1.5–2 kA/cm^2. The device lased for a few seconds at the beginning of the test. Formation of triangular nonluminescent dark defects in the laser stripe region was observed by EL microscopy performed through the ITO contacting material.

Following degradation, the microstructure of the device was studied using plan-view TEM in a JEOL 2000EX transmission electron microscope at 200 kV. The TEM sample was prepared by ion milling the device from the bottom of the GaAs substrate first until a perforation was made. The sample was also ion milled gradually from the top side to achieve electron transparency. The edge of each interface between two adjacent layers around the perforation was observed as a line in the plan-view TEM images. Based on those lines, each particular layer which remained in the TEM sample after each ion milling was identified.

Areas that are away from the laser stripe region, and therefore are nondegraded, were investigated first. Misfit dislocations in this particular imperfectly lattice-matched laser sample were observed at the p-ZnMgSSe (cladding)/p-ZnSSe (waveguiding) interface, although the average spacing between them was found to be larger than 50 μm. No misfit dislocations were observed at other interfaces, except for those within the Zn(Te,Se) graded layer ohmic contact region which is highly lattice mismatched. Pairs of V-shaped stacking faults and associated threading dislocations were observed as the most commonly observed type of defects present in the structure. In the degraded laser stripe region, patches of defect networks were observed.

Figure 1 is a representative TEM bright field image showing a part of such a defect network. Weak-beam imaging using the reflection $g=2\bar{2}0$ with the reflection $3g$ operating indicated that the networks consist mainly of dislocation dipoles. The dislocation dipoles are elongated mainly along two directions. It is not clear at present whether these dipoles are of the interstitial type or of the vacancy type; it is unclear whether they contain a fault. Three nearly vertical dark bands are seen in the right-hand part of Fig. 1. They

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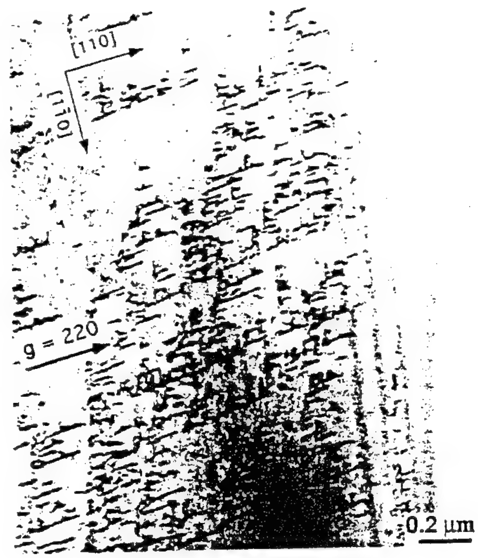

FIG. 1. Bright field image showing a part of a patch of a dislocation network.

have been identified to be the edges of the three QWs in the wedge-shaped plan-view TEM sample. Only the area on the left-hand side of the dark bands includes the QWs. The dislocation network starts to show at the edges of the QWs, which indicates that the network is localized at the QW region.

Figures 2(a) and 2(b) are two bright field images taken from the same area. The ends of two patches of dislocation networks [marked D1 and D2 in Fig. 2(a) only] are observed in the images. D1 is the end of the same dislocation network as is shown in Fig. 1, while D2 is the end of another dislocation network. The two patches of dislocation networks are much denser at the end area, and they are well bounded along two directions, which are nearly the [340] and [$\bar{3}$40] directions. Dislocation networks bounded along nearly the [430] and [4$\bar{3}$0] directions have also been observed. These directions are in agreement with the two sharp edges of the triangular dark defects observed in our EL microscopy images.[9] Therefore, we identify the dislocation networks with the triangular dark defects observed in EL.

It is observed in Fig. 2 that each of the two dislocation networks originates from a dislocation [marked T1 or T2 in Fig. 2(a) only] which in turn starts from a pair of V-shaped stacking faults (S1 and S2). [In Fig. 2(b) the contrast from the two stacking faults vanishes due to the diffraction condition, while the partial dislocations bounding them are clearly observed.] As mentioned before, this type of defect complex, consisting of a pair of V-shaped stacking faults together with associated threading dislocations, is the most commonly observed defect present in the device structure, also including the nondegraded areas that are as far away from the laser stripe as 0.25 mm. Therefore, these defect complexes are believed to represent defects formed during the MBE growth. Their density is estimated to be in the middle $10^5/cm^2$ range.

The three-dimensional arrangement of the defects shown in Fig. 2 has been investigated by using TEM stereo micros-

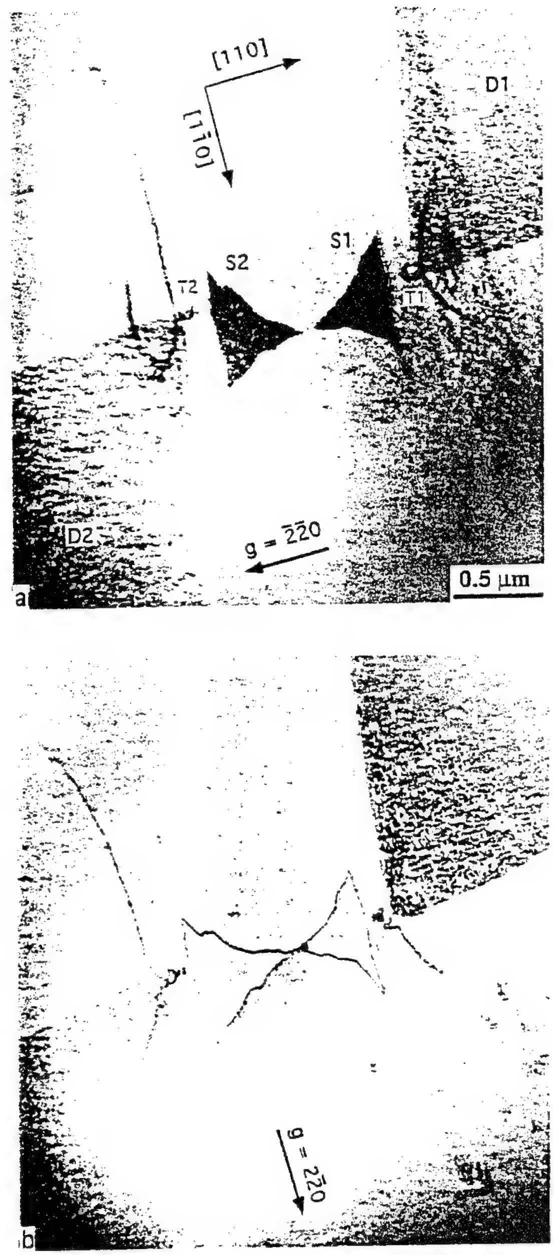

FIG. 2. Bright field images (of the same area but with two orthogonal reflections operating) showing two patches of dislocation networks (D1 and D2). These are nucleated at threading dislocations (T1 and T2) which originate at a pair of V-shaped stacking faults (S1 and S2).

copy. Two bright field images used as a stereo pair were taken with the same reflection $g=\bar{2}\bar{2}0$ operating, but with the electron beam incident direction about 5° off from the [001] direction toward the [$\bar{1}$12] and the [1$\bar{1}$2] directions, respectively. The result is schematically shown in Fig. 3. The two patches of dislocation networks were observed to reside at the same depth level, which is the QW region, as mentioned before. The two stacking faults appear to begin at or near the II-VI/GaAs interface and end at the n-ZnSSe/n-ZnMgSSe interface. Here, the depth in the structure over which the stacking faults extend was derived from the dimensions observed from the [001] direction, since we know that the stacking faults lie on the (11$\bar{1}$) and (111) planes, respectively. Contrast analysis of Fig. 2(b) indicates that the partial dislo-

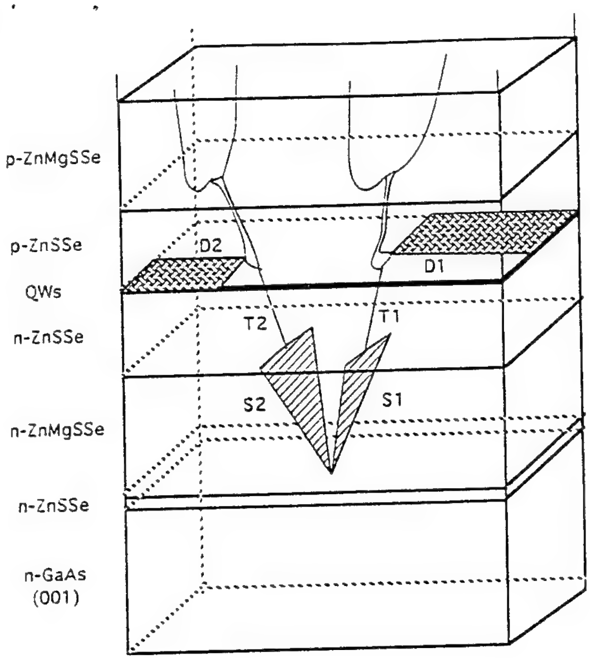

FIG. 3. Schematic showing the three dimensional arrangement of the defects shown in Fig. 2.

cations bounding the stacking faults are Shockley partial dislocations with the Burgers vector $b=1/6\langle 112\rangle$. The two partial dislocations bounding each of the stacking faults unite at the n-ZnSSe/n-ZnMgSSe interface to form a perfect (or narrowly dissociated) dislocation having the Burgers vector $b=1/2[1\bar{1}0]$ and threading upwards. When the dislocation reaches the QW region, as can be seen in Figs. 2(a) and 2(b), it appears that the dislocation starts to dissociate widely again, resulting in formation of a small stacking fault starting at that region. We note that dissociation at the QW region of the dislocations starting from the V-shaped stacking faults has also been confirmed for more than ten of these of defect complexes observed in the nondegraded areas. The defect finally becomes a dislocation half-loop at or near the p-ZnMgSSe/p-ZnSSe interface, and threads upwards. The detailed dislocation reaction near the p-ZnMgSSe/p-ZnSSe interface is not clear at present.

The formation of the dislocation networks developed at the QW region can be explained by climb motion of the dislocations penetrating the QW region. Since the dislocation networks were observed only in the laser stripe region, it can be concluded that the dislocation climb motion was probably enhanced by carrier recombination during the current injection, as suggested for the formation of dislocation networks in degraded GaAlAs/GaAs double-heterostructure (DH) lasers.[10] Unlike the situation in lattice-matched GaAlAs/GaAs DH laser structures, the active QW region in the present ZnCdSe/ZnSSe/ZnMgSSe SCH configuration contains large compressive lattice strain. This compressive lattice strain may be responsible for the dissociation of the dislocations (e.g., T1 and T2 in Figs. 2 and 3) in the QW region. If the dipoles in the dislocation networks observed in the present ZnCdSe/ZnSSe/ZnMgSSe SCH laser structure are composed of vacancies, formation of them may contribute to the relief of the compressive lattice strain in the QW region.

In summary, we have carried out a detailed microstructural study of a particular degraded blue-green laser device fabricated from the ZnCdSe/ZnSSe/ZnMgSSe SCH configuration by TEM. Triangular nonluminescent dark defects observed by EL microscopy in the laser stripe region have been identified to be patches of dislocation networks developed at the QW region. The networks consist mainly of dislocation dipole branches elongated nearly along the ⟨430⟩ directions when projected to the (001) plane. Complexes of defects consisting of a pair of V-shaped stacking faults which are nucleated at or near the II-VI/Gas interface, and associated threading dislocations, have been observed as the most commonly observed defects present randomly throughout this SCH laser structure, including nondegraded areas. These defect complexes are believed to represent defects formed during the MBE growth. The dislocation networks have been observed to be nucleated at such complexes of defects. The results suggest the importance of eliminating point defects as well as stacking faults and threading dislocations in the laser structures. Subsequent structures having modified growth of the QW region (primarily higher growth temperature to reduce point defects) exhibited a reduced tendency for the generation of dark defects, and resulted in the room temperature cw operation cited above.

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APPENDIX E

D (donor) X center behavior for holes implied from observation of metastable acceptor states

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The observation of persistent photoconductivity in nitrogen-doped p-ZnMgSSe at low temperature is reported. The increase of conductivity after illumination appears due to a metastable population of holes which are in thermodynamic equilibrium with hydrogenic acceptors having reduced activation energy. The experimental evidence suggests the presence of a DX-like [D (donor) X center] behavior for holes. © *1994 American Institute of Physics.*

Low-resistivity p-type ZnSe was first reported in 1990[1,2] as the result of employing an rf nitrogen plasma source during growth by molecular beam epitaxy (MBE). The capability of achieving amphoteric conductivity in ZnSe and Zn(S,Se) was one of the key factors responsible for the demonstration of blue/green diode lasers in 1991,[3,4] though at that time the laser operation was confined to cryogenic temperature, or at room temperature under pulsed excitation. The proposal by Okuyama *et al.*[5] for adding group IIA Mg into Zn(S,Se) provided opportunities for simultaneous lattice matching (to GaAs) with band gap widening/tuning through control of alloy fractions. Pseudomorphic separate confinement heterostructure (SCH) lasers based on this novel quaternary were subsequently implemented.[6] Brief room-temperature continuous-wave (cw) operation was reported[7,8] from such structures when employing a Zn(Se,Te) pseudo-graded contact to p-ZnSe.[9]

Since the ohmic behavior of the graded contacting scheme is maintained down to cryogenic temperatures,[10] the Zn(Se,Te) contact provided an opportunity to investigate the electrical transport properties of p-type ZnSe. The study of temperature-dependent Hall measurements led the authors to speculate that the transport behavior of nitrogen acceptors in p-ZnSe supports a hydrogenic effective-mass model.[10] In addition, it was subsequently noted (Fig. 1) that the apparent activation energy increases quite rapidly (from 90 to 177 meV) as the host material changes from binary ZnSe (E_G~2.8 eV at 10 K) to quaternary $Zn_{0.93}Mg_{0.07}S_{0.14}Se_{0.86}$ (E_G~2.96 eV at 10 K).[11] The magnitude of change presents a significant deviation from an effective-mass model where changes are simply due to variations of material parameters. Following previous interpretations of similar trends observed for some p-type dopants in III–V alloys, the increase in apparent activation energy was tentatively attributed to central-cell corrections.[11] At the same time we speculated that the appearance of the second freeze-out slope (ZnMgSSe curve in Fig. 1) indicated the presence of a shallower acceptor of much lower concentration.

The observed rapid "deepening" of the acceptor activation energy (E_a) for the nitrogen dopant in wider band gap alloys of ZnSe contributes directly to the magnitude of existing device impedances. As a result, the drastic increase of E_a from binary to quaternary imposes serious limitations on the exploration of shorter wavelength diode laser configurations employing higher Mg and S fractions. In this letter we address two issues relative to the p-type nitrogen doping of the wide band gap quaternary alloy, namely the exploration of the origin of the second shallower level observed at low temperatures, and an explanation for the rapid increase of acceptor activation energy over that of ZnSe. The observation of persistent photoconductivity (PPC), the appearance of a metastable shallow hydrogenic level, and the large difference between the thermal and optical ionization energies, taken together suggest that the observed deepening of the nitrogen level in the alloy system is due to a shallow-deep transition through a lattice relaxation around the impurity atom, a phenomenon quite similar to the so-called "D (donor) X center" behavior observed in many n-type III–V and II–VI semiconductors.[12] Such DX center phenomenon is often described as a manifestation of the extrinsic self-trapping[13] of electrons. In previous reports we have described, in the context of photoluminescence measurements, the extrinsic self-trapping of photoexcited holes in connection with the isoelectronic doping of ZnSe with Te.[14]

The transport measurements were performed on nomi-

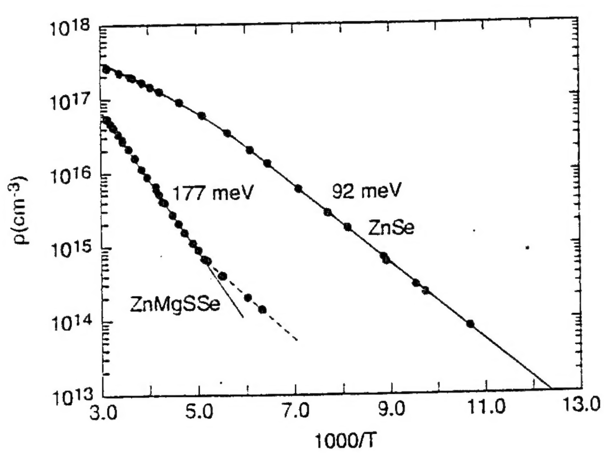

FIG. 1. Free-hole concentration vs inverse temperature for nitrogen-doped ZnSe and ZnMgSSe epilayers. The apparent activation energy values obtained from the carrier freeze-out is labeled.

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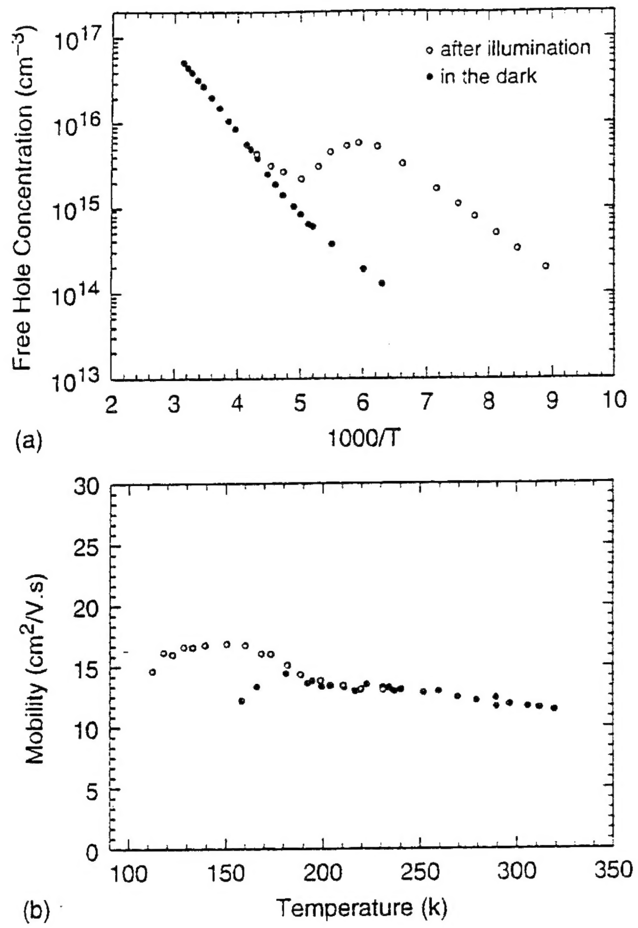

FIG. 2. (a) Free-hole concentration and (b) Hall mobility vs inverse temperature for a ZnMgSSe epilayer. The solid dots represent data taken in the dark. The second slope in the Arrhenius plot of free-hole concentration, which appears below some critical temperature, is interpreted to represent the presence of a shallow hydrogenic acceptor state. The photoionization occurring under illumination for photons above 1.65 eV results in a metastable persistent photoconductivity supported by free holes in thermodynamic equilibrium with the shallow acceptor state.

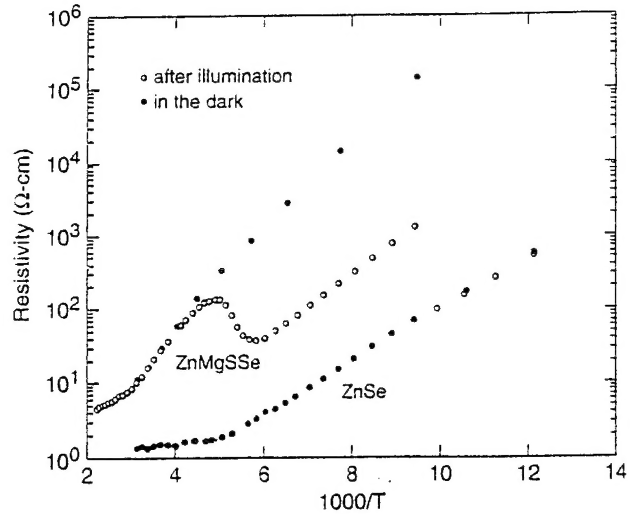

FIG. 3. Resistivity of a rectangular bar vs inverse temperature. The persistent photoconductivity in the quaternary is associated with a drop in resistivity of more than two orders of magnitude. Under similar illumination, the ZnSe epilayer shows about a 10% reduction in resistivity at low temperature.

nally 2 μm thick nitrogen-doped p-type ZnSe and ZnMgSSe epilayers grown on semi-insulating GaAs by MBE. Details of the epitaxial growth procedure,[15] the design and growth of the Zn(Se,Te) graded layer contacts,[9] and the preparation of Van der Pauw samples[10] have been described previously. In addition to the temperature-dependent Hall measurements (whose maximum temperature was limited to 320 K), independent resistivity measurements were performed in a variable-temperature probe station from 100 to 450 K on samples with a well-defined rectangular geometry. Optical illumination was provided by a tungsten lamp with excitation wavelength selected through a Bausch & Lomb monochromator. Various filters were employed to ensure the blockage of the higher-order harmonics; the illumination intensity was monitored using a calibrated Si detector.

Figure 2(a) shows an Arrhenius plot for the free-hole concentration of a ZnMgSSe epilayer, obtained from Hall data, in which the appearance of two slopes ($E_{a1}=177$ meV and $E_{a2}=90$ meV) along the freeze-out curve obtained in the dark (solid circles) is observed. For this sample secondary ion mass spectroscopy (SIMS) shows a nitrogen concentration [N] of approximately 1.0×10^{18} cm^{-3}. Upon illumination of the sample with wavelengths shorter than 750 nm ($E_\lambda>1.65$ eV) at 110 K, the hole concentration increased by orders of magnitude and persisted (in the dark) during the first part of a warm-up process. In contrast, the photoconductivity remained practically unchanged even under prolonged (on the order of minutes) exposure to photons when the irradiation wavelength was longer than 900 nm. The gradual increase of the hole concentration during heating (open circles) is characterized by a linear dependence with a slope that indicates a shallower level, and one having a similar activation energy to that obtained from Hall measurements (in the dark) on ZnSe:N (Fig. 1). Further insight into the transport behavior was obtained through the resistivity measurement from 100 to 450 K, as shown in Fig. 3. Persistent photoconductivity, with a resistivity decrease of more than two orders of magnitude, is again observed at low temperature. As a comparison to the quaternary alloy, an identical illumination experiment performed on nitrogen-doped ZnSe shows approximately a 10% reduction in the sample resistivity at low temperatures (Fig. 3).

Phenomenological comparisons between the behavior of n-type III–V compounds and the evidence reported here tend to support the assertion that nitrogen acceptors in p-ZnMgSSe possess a DX nature; the proposed relaxed state here should perhaps be called an "A(acceptor)X center". DX centers are characterized by a large difference between the thermal (derived from temperature-dependent Hall measurements) and optical ionization energies; this is taken to imply that impurity atoms undergo strong coupling to the host lattice.[12] The deep localized DX level and its tetrahedral hydrogenic manifestation are separated by capture and emission barriers as a result of phonon coupling. The appearance of the second, less steep freeze-out slope, observed in the dark below the critical temperature T_c, signifies that the

freeze-out of holes into the deep localized levels (AX centers) is inhibited by the thermal capture barrier[16] associated with the lattice relaxation. Below T_c, and in the dark, the interaction between free holes and the relatively shallow hydrogenic level becomes the only allowed exchange, hence, the reduced slope of the freeze-out characteristics below T_c. Illumination at low temperature (with photon energies greater than the optical ionization energy) converts the localized deep states into shallow hydrogenic levels. Below T_c, thermal equilibrium, wherein the population of these two states (deep and shallow) would follow Fermi–Dirac statistics, cannot be reached due to the "isolation" produced by the thermal capture barrier. The capture barrier thus facilitates a low-temperature, metastable population of holes which are restricted to the valence-band-hydrogenic acceptor combination; the result is the observed persistence of photoconductivity. The similarity of the value of E_a for the shallower level of ZnMgSSe:N to that of ZnSe:N provides compelling evidence that both originate from the hydrogenic effective-mass impurity level.

The warm-up characteristics of the hole concentration after illumination offers further insight into the origin of the PPC, as the observation of PPC alone is known to be a necessary (but not sufficient) condition for concluding the existence of DX centers.[12] The initial linear increase of the PPC with increasing temperature (as opposed to a constant or decreasing dependence) is an effect which seems not readily accounted for by models for PPC involving carrier separation due to macroscopic potential barriers,[17] but is certainly consistent with the presence of microscopic barriers due to lattice relaxation. In fact the warm-up process below T_c can be modeled precisely[18] as a p-ZnMgSSe sample doped with only shallow nitrogen acceptors, specifically with E_a of 90 meV. When the temperature exceeds T_c, the lattice relaxation again occurs and the AX centers start to dominate the electrical transport.

The rapid increase of nitrogen E_a from ZnSe to ZnMgSSe appears to be in close analogy to the behavior of substitutional donors in the GaAs–AlGaAs system.[12] The implication is that the "deepening" observed in the II–VI system is likely a reflection of the relative positioning between the Γ-point valence-band edge (sensitive to the alloy composition) and the highly localized deep state (less sensitive to the alloy composition). The addition of Mg and S to ZnSe has the effect of pushing the valence-band edge (and the hydrogenic acceptor level) downward, and causes the observation of the AX level (now lying within the band gap) to be energetically more favorable.[19] In fact such a correspondence between n-AlGaAs and p-Zn(Mg)S(Se):N can be viewed as having been anticipated by the theoretical model for large lattice relaxation presented by Chadi and Chang[20] in the context of their discussion of the traditional difficulty in obtaining p-ZnSe.

In summary, we have investigated the issue of acceptor activation in p-type ZnMgSSe. It was found that the rapid increase of activation energies from ZnSe to the quaternary seems consistent with a lattice relaxation model similar to DX centers in n-type AlGaAs. The observation of persistent photoconductivity, a second metastable hydrogenic level, and the large difference between thermal and optical depths provide support for such an assertion. In light of the experiments described here, it is notable that the concluding remarks in a recent review of DX centers raised the question of why DX-like behavior had not, at that point, been observed for holes.[12] It seems unlikely that nitrogen-doped ZnMgSSe is the only material system so far with p-type AX center behavior. Interest in this material in the context of blue/green light emitters mandates seeking means to eliminate AX centers.

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